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Production of sunflower oil methyl esters by optimized alkali-catalyzed methanolysis

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ABSTRACT

We report the optimization of sunflower oil methyl esters (SOME/biodiesel) production via alkaline catalyzed transesterification of crude sunflower oil and subsequent physical and chemical characterization. The optimum conditions elucidated for the methanolysis of sunflower oil were found to be: methanol/sunflower oil molar ratio, 6:1; reaction temperature, 60 °C; and NaOH catalyst concentration, 1.00% (w/w). An optimum SOME yield of 97.1% was achieved. SOME were analyzed by gas–liquid chromatography (GLC). A number of fuel properties of SOME as measured according to accepted methods were found to satisfy nearly all prescribed ASTM D 6751 specifications, where applicable. The results of the present study indicated that SOME could be a potential alternative to other common biodiesels and petrodiesel.

1. Introduction

Biodiesel, defined as the simple monoalkyl esters of fatty acids derived from vegetable oil, animal fat, or waste oils, is an interesting and environmentally friendly alternative to conventional diesel fuel (CDF) for combustion in compression-ignition (diesel) engines. Biodiesel is produced by transesterification of a triglyceride with methanol in the presence of catalyst to produce fatty acid methyl esters (FAME) and glycerol. Transesterification employing alkali catalysis and short-chain alcohols provides a high level of conversion. The main parameters affecting the transesterification reaction are molar ratio of vegetable oil to alcohol, catalyst type and amount, reaction time and temperature, and the contents of free fatty acids (FFAs) and water in substrate oil [1]. A number of alkaline catalysts are in practice for transesterification of triglycerides, such as NaOH, KOH, sodium and potassium alkoxides, and carbonates [2]. For alkali-catalyzed transesterifications, the triglyceride must contain relatively low levels of FFAs and the alcohol used is essentially anhydrous. Otherwise, unwanted soap formation and ester hydrolysis may occur [1,3,4]. In cases where triglycerides contain high levels of FFAs, acid catalysis may be necessary to avoid pretreatment [5]. Methanol is normally the alcohol of choice for biodiesel production because it is inexpensive and affords a high level of conversion [2].

Sunflower (*Helianthus annuus* L.), a member of the *Compositea* family is an important oilseed crop worldwide, yielding approximately 45–50% oil (dehulled seed mass basis). In Pakistan, sunflower, considered as a non-conventional

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oilseed crop is generally grown in two seasons, spring and summer. In wide range climatic conditions of Pakistan, sunflower crop fits well in the local intercropping systems and could be successfully grown in spring and fall thus yielding two crops in 1 year [6]. A huge potential exists to increase the domestic production of sunflower in Pakistan. Recently, serious efforts have been made to encourage the local production of this crop. As a result, the sunflower acreage has increased from 107,717 ha in 2002–03 to 379,204 ha in 2006–07. The current sunflower seed and oil production in Pakistan is 656,000 and 249,000 tons, respectively [7].

Sunflower oil, widely used in foods for cooking and frying purposes, is also gaining attention as a feedstock for biodiesel production. Antolin in 2002 [8] reported the transesterification of sunflower oil with methanol, examining the effects of alcohol, catalyst amount, and reaction temperature. The following optimized conditions were obtained: alcohol:oil molar ratio of 9:1; 0.28% (w/w) KOH catalyst; and 70 °C reaction temperature. There is no previously reported sufficient data on optimization of conditions for the methanolysis of sunflower oil. Therefore, the main objectives of the present work were to optimize the type and concentration of catalyst, molar ratio of alcohol to oil, and reaction temperature for the transesterification of sunflower oil. The resultant sunflower oil methyl esters (SOME) were characterized and a number of important fuel properties were determined and compared.

2. Materials and methods

Sunflower (*H. annuus*) seeds (variety viz. FH-330), harvested by mid of November 2006 were procured from Ayub Agricultural Research Institute (AARI), Faisalabad, Pakistan. The seeds stored in storage room of AARI at ambient and collected after about 1 month of the harvest were not further stored prior to extraction in the experimental lab. Pure standards of FAME were obtained from Sigma Chemical Company (St. Louis, MO). All other chemicals and reagents were analytical reagent grade and purchased from Merck Chemical Company (Darmstadt, Germany).

2.1. Extraction of sunflower oil

Sunflower seeds (500 g) were crushed using a commercial grinder and fed to a Soxhlet extractor fitted with a 2 L round bottomed flask. The extraction was executed on a water bath for 6 h with *n*-hexane. The solvent was removed at 45 °C under vacuum using a rotary evaporator (Eyela, N-N Series, Rikakikai Co. Ltd., Tokyo, Japan).

2.2. Transesterification of sunflower oil

The experimental variables examined in this study were methanol oil molar ratio, catalyst type, catalyst concentration, and reaction temperature. The amount of sunflower oil, reaction time, alcohol type, and rate of agitation were fixed through the experiments. Transesterification of sunflower was carried out in a 1 L round bottomed reactor equipped with a thermostat, mechanical stirrer, sampling outlet, and condensation system. Briefly, sunflower oil (500 g) was preheated to the set temperatures (30, 45, or 60 °C) on a heating plate prior to starting the reaction. A fixed amount of freshly prepared methanolic solutions of the selected catalysts (NaOH, KOH, $NaOCH_3$, or $KOCH_3$) were added into the reactor, and mixed, accounting this moment as time zero of the reaction. At 20 min intervals, 2 μL samples were withdrawn for gas–liquid chromatography (GLC) analysis. Each experiment was allowed to proceed for 120 min with agitation (600 rpm). After the completion of the reaction, the reaction mixture was allowed to cool to room temperature and equilibrate, resulting in the separation of two phases. After separation of the two phases by sedimentation, the upper SOME phase was purified by distilling at 80 °C to remove excess methanol, followed by successive washes with distilled water and treatment with Na_2SO_4 and filtration. The lower glycerol layer was acidified with concentrated H_2SO_4 to neutralize any unreacted catalyst and decompose the soaps formed during the transesterification. The resulting mixture was subjected to distillation at 80 °C under moderate vacuum to recover the excess methanol thus purifying the glycerin.

2.3. Characterization and quality evaluation of SOME

Analysis of SOME was carried out employing a Shimadzu (Kyoto, Japan) Model 17-A GC equipped with a flame ionization detector and a methyl-lignocerate-coated polar capillary column SP-2330 (30 m × 0.32 mm, 0.20 μm; Supelco Inc., Supelco Park Bellefonte, PA). Carrier gas was N_2 at 4.0 cm^3/min. The oven temperature was initially held at 180 °C for 2 min, then increased to 220 °C at a ramp rate of 3 °C/min, followed by a 10 min hold period. The injector and detector temperatures were set at 230 and 250 °C, respectively. A sample volume of 1 μL was injected using split mode. FAME were identified by comparing their relative and absolute retention times to those of pure standards. The FAME composition was reported as a relative percentage of the total peak area.

A number of important fuel properties of SOME as specified in Table 3 were determined following recommended ASTM [9] and CEN [10] methods.

3. Results and discussion

3.1. Reaction temperature

The transesterification of sunflower oil was carried out at 30, 45, and 60 °C in order to evaluate the effect of reaction temperature on SOME production. The constant reaction time of 120 min, 1.0% (w/w) of $NaOCH_3$ catalyst, methanol:oil molar ratio of 6:1, and agitation intensity of 600 rpm were maintained with the temperature variations for the production of SOME. The transesterification was proceeded to more than 80% completion after 10 min, regardless of the temperature variations. As indicated by Table 2, after 120 min, the reaction was completed up to 97.1%, 92.8%, and 90.9% at 60, 45, and 30 °C, respectively. As such, it is recommended that methanolysis/transesterification of sunflower oil can be performed at 60 °C, which is in agreement with the previous literature report [11], which indicates that base-catalyzed

transesterification of vegetable oils are most efficient near the boiling point (bp) of the alcohol (methanol bp 65 °C). Our results were somewhat varied to Antolin et al. [8] who investigated an optimum reaction temperature of 70 °C for production of biodiesel by transesterification of sunflower oil.

3.2. Catalyst type and amount

The effect of catalyst type on SOME production was ascertained in four experiments (NaOH, KOH, $NaOCH_3$, and $KOCH_3$) at 1.00% (w/w) of catalyst concentrations. In all four experiments a methanol:oil molar ratio, 6:1; agitation intensity, 600 rpm; and reaction temperature, 60 °C were employed. As can be seen from Table 2, the optimum yield of SOME (97.1%) was achieved with NaOH catalyst, which is in agreement to the results of Encinar et al. [12], obtained in the methanolysis and ethanolysis of *Cynara cardunculus* L. oil.

In an effort to investigate the effect of catalyst amount on SOME production, a series of seven experiments were designed with varying NaOH concentrations (0%, 0.25%, 0.50%, 0.75%, 1.00%, 1.25%, 1.50% w/w). The methanol:oil molar ratio, agitation intensity, and reaction temperature employed were the same as utilized in the previous four experiments. As shown in Table 2, the optimum yield (97.1%) of SOME was achieved with a concentration of 1.00% NaOH (on the basis of weight of raw oil). As expected, no product was obtained with 0% catalyst. Higher catalyst concentrations, such as 1.25% and 1.50%, had detrimental effects on SOME yield and quality, which is in accordance with previous reports on the methanolysis of *Brassica carinata* [13] and rapeseed oil [14], and the methanolysis and ethanolysis [12] of *C. cardunculus* L. oil. Conversely, Antolin et al. [8] concluded that 0.28% KOH (70 °C) is the optimum catalyst amount in the transesterification of sunflower oil.

3.3. Methanol/oil molar ratio

The methanol/oil molar ratio (3:1, 6:1, 9:1, 12:1, 15:1, and 18:1) was varied in six experiments to determine the effect of methanol amount on SOME production. In all experiments, 600 rpm agitation intensity, 60 °C reaction temperature, and 1.0% NaOH concentration were employed. As can be seen from Table 2, the optimum yield (97.1%) of SOME was achieved with a molar ratio of 6:1. The stoichiometric ratio of methanol:oil, 3:1, provided the lowest conversion (61.5%). An increase in the ratio of methanol/oil beyond 6:1, even up to 18:1 did not result in higher SOME yields (data not shown). In fact, higher quantities of methanol had a detrimental effect on SOME yield, as indicated by steadily reducing SOME yields when the methanol/oil molar ratios increased from 6:1 to 18:1. Antolin et al. [8] investigated optimum conversion of sunflower oil to methyl esters at 70 °C with a methanol/oil molar ratio of 9:1, using 0.28% of KOH as catalyst. Variations in our analysis might be attributed to the differences of reaction temperature, catalyst type and concentration, and the varied nature of sunflower oil used.

3.4. Characterization and quality of optimized SOME

The fatty ester profile of SOME, as determined by GC and depicted in Table 1, was typical. Shown for comparison (Table 1) are other common biodiesel fuels, including rapeseed methyl esters (RME), soybean oil methyl esters (SME), and palm oil methyl esters (PME). The main methyl ester was linoleic acid (55.2%), followed by oleic (33.2%), palmitic (7.0%) and stearic (3.5%) acids (Table 1).

The present GC analysis supported the fact that SOME produced under optimized protocol had its free and total glycerol contents with in ASTM D 6751 specifications (Table 3). Non-optimized methanolysis experiments yielded impure SOME with sizeable residual amounts of free and total glycerol. The quality of optimized SOME was verified by the determinations as shown in Table 3. The determined acid

Table 1 – Fatty acid methyl ester (FAME) profile (relative %) of SOME, with RME, SME, and PME shown for comparison

FAME	SOME	RME[a]	SME[a]	PME[a]
C16:0	7.0±0.2	4	11	44
C18:0	3.5±0.1	2	4	4
C18:1	33.3±0.6	56	22	40
C18:2	55.2±0.4	26	53	10
C18:3	tr	10	8	tr
Other	1.0±0.1	2	2	2

Values are mean±SD of triplicate determinations.
[a] From Ref. [15].

Table 2 – Average sunflower oil methyl ester (SOME) yield in alkali-catalyzed transesterification of sunflower oil under different treatments (120 min reaction time, 600 rpm agitation rate)

Reaction temp (°C)	Methanol:oil molar ratio	Catalyst (wt%)	Catalyst type	SOME yield (%)
60	6:1	1.00	KOH	86.7±0.9
60	6:1	1.00	$KOCH_3$	90.0±0.7
60	6:1	1.00	$NaOCH_3$	82.7±1.1
30	6:1	1.00	NaOH	90.9±0.8
45	6:1	1.00	NaOH	92.8±1.0
60	6:1	1.00	NaOH	97.1±0.9
60	3:1	1.00	NaOH	61.5±0.7
60	9:1	1.00	NaOH	93.0±1.2
60	12:1	1.00	NaOH	86.0±1.5
60	15:1	1.00	NaOH	83.8±1.2
60	18:1	1.00	NaOH	81.0±0.8
60	6:1	0.25	NaOH	51.6±1.0
60	6:1	0.50	NaOH	65.0±0.8
60	6:1	0.75	NaOH	92.9±0.9
60	6:1	1.25	NaOH	82.7±1.5
60	6:1	1.50	NaOH	78.1±1.2

Values are mean±SD of triplicate determinations.

Table 3 – Fuel properties of SOME

	Method[a]	SOME
Specific gravity (15 °C)	D 287	0.88±0.03
Kinematic viscosity (40 °C, mm^2/s)	D 445	4.90±0.20
High heating value (MJ/kg)	D 4868	45.3±1.2
Flash point (°C)	D 93	170.0±3.0
Combustion point (°C)	D 92	178.0±2.7
Cold filter plugging point (°C)	D 6371	−1.0±0.1
Cloud point (°C)	D 2500	1.0±0.1
Pour point (°C)	D 97	−4.0±0.2
Sulfur content (%)	D 4294	0.012±0.001
Ash content (%)	D 874	0.010±0.001
Water content (%)	D 95	<0.01
Copper strip corrosion (50 °C, 3 h)	D 130	1a
Oxidation stability (110 °C, h)	EN 14112	2.0±0.1
Lubricity (μm)	D 6079	142±1.5
Acid value (mg KOH/g)	D 664	0.24±0.02
Free glycerin (%)	D 6584	0.015±0.001
Total glycerin (%)	D 6584	0.201±0.010

Values are mean±SD of triplicate determinations.
[a] D methods: ASTM; EN method: European Committee for Standardization.

value (AV, 0.24 mg KOH/g), sulfur content (0.012% by mass), free glycerin (0.015% by mass), total glycerin (0.201% by mass), ash content (0.010% by mass), and water content (<0.01% by mass) of SOME were found to be within prescribed ASTM D 6751 specifications.

As expected, SOME exhibited excellent lubricity (142 μm), as determined by the high-frequency reciprocating rig (HFRR) method according to ASTM D 6079. Oxidation stability of SOME as measured following the Rancimat method (EN 14112), provided an induction period (IP) of 2.0 h. This value is lower than the minimum IP specified in ASTM D 6751 (⩾3 h), which may be attributed to the relatively high C18:2 content of SOME (Table 1). Treatment with antioxidant additives may restore the oxidative stability of SOME to an acceptable level. All other properties of SOME, depicted in Table 3, satisfied the prescribed ASTM D 6751 specifications. Our results are in agreement with a previous study which indicates that fuel properties of SOME are generally with in ASTM D 6751 specifications [8].

4. Conclusion

Results of present study demonstrated that the optimum conditions elucidated for the methanolysis of sunflower oil were: 6:1 molar ratio of sunflower oil to methanol, 60 °C reaction temperature, and 1.00% (w/w) NaOH catalyst. The optimized conditions provided SOME in high yield (97.1%). The fuel properties of SOME measured were also within prescribed ASTM D 6751 specifications, thus indicating that SOME is acceptable as a substitute for other common biodiesel and petrodiesel fuels for combustion in compression-ignitions (diesel) engines.

Disclaimer

Product names are necessary to report factually on available data; however, the USDA neither guarantees nor warrants the standard of the product, and the use of the name by USDA implies no approval of the product to the exclusion of others that may also be suitable.

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